2 Classification

In this chapter mathematical models are classified by

- grouping into opposite pairs;
- mathematical complexity;
- degree of resolution.

The intention is to give the reader an understanding of differences between models as reflected by the modeling goal. Which question is the model intended to answer?

2.1 Grouping of models into opposite pairs

In this section, we will examine various types of mathematical models. There are many possible ways of classification. One possibility is to group the models into opposite pairs:

- linear versus nonlinear;
- steady state versus non-steady state;
- lumped parameter versus distributed parameter;
- continuous versus discrete variables;
- deterministic versus stochastic;
- interpolation versus extrapolation;
- mechanistic versus empirical;
- coupled versus not coupled.

Linear versus nonlinear

Linear models exhibit the important property of superposition; nonlinear ones do not. Equations (and thus models) are linear if the dependent variables or their derivatives appear only to the first power; otherwise they are nonlinear. In practice, the ability to use a linear model for a process is of great significance. General analytical methods for equation solving are all based on linearity. Only special classes of nonlinear models can be attacked with mathematical methods. For the general case, where a numerical method is required, the amount of computation is also much less for linear models, and in addition error estimates and convergence criteria are usually derived under linear assumptions.

Steady state versus transient

Other synonyms for steady state are time invariant, static, or stationary. These terms refer to a process in which the point values of the dependent variables remain constant over time, as at steady state and at equilibrium. Non-steady-state processes are also called unsteady state, transient, or dynamic, and represent a situation in which the process dependent variables change with respect to time. A typical example of an non-steady-state process is the startup of a distillation column which would eventually reach a pseudosteady-state set of operating conditions. Inherently transient processes include fixed-bed adsorption, batch distillation, and reactors, drying, and filtration/sedimentation.

Lumped parameter versus distributed parameter

A lumped-parameter representation means that spatial variations are ignored, and the various properties and the state of a system can be considered homogeneous throughout the entire volume. A distributed-parameter representation, in contrast, takes into account detailed variations in behavior from point to point throughout the system. All real systems are, of course, distributed in that there some variations occur throughout them. As the variations are often relatively small, they may be ignored, and the system may then be "lumped."

The answer to the question whether or not lumping is valid for a process model is far from simple. A good rule of thumb is that if the response of the process is "instantaneous" throughout the process, then the process can be lumped. If the response shows instantaneous differences throughout the process (or vessel), then it should not be lumped. Note that the purpose of the model affects its validity. Had the purpose been, for example, to study mixing in a stirred tank reactor, a lumped model would be completely unsuitable because it has assumed from the first that the mixing is perfect and the concentration a single variable.

Because the mathematical procedures for solving lumped-parameter models are simpler than those for solving distributed-parameter models, we often approximate the latter using an equivalent lumped-parameter system. Whilst lumping is often possible, we must be careful to avoid masking the salient features of a distributed element and subsequently building an inadequate model by lumping.

As an example of the use of lumped versus distributed mathematical models, consider the equilibrium stage concept of distillation, extraction, and similar processes. As shown in Figure 2.1, we usually assume that the entire stage acts as a whole, and we do not consider variations in temperature, composition, or pressure in various parts of the stage. All of these variables are "lumped" together into some overall average. The errors introduced are compensated for by the stage efficiency factor.

Continuous versus discrete variables

Continuous means that the variables can assume any values within an interval; discrete means that a variable can take on only distinct values within an interval. For example, concentrations in a countercurrent packed bed are usually modeled in terms of continuous variables, whereas plate absorbers are modeled in terms of staged multicompartment

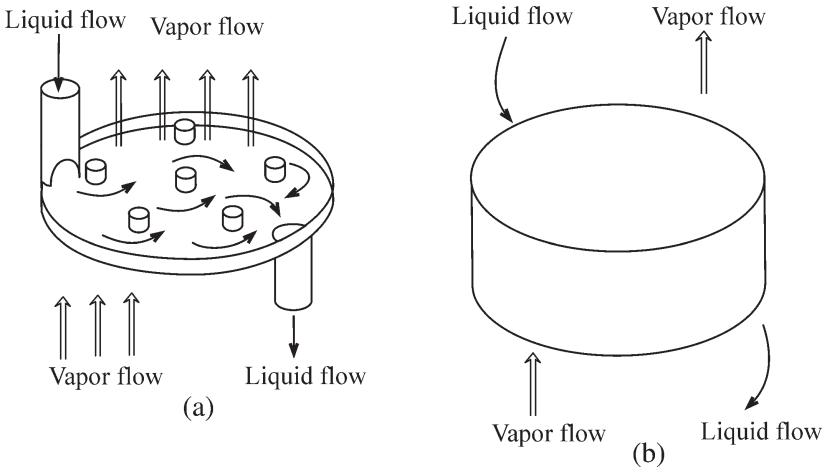

Figure 2.1. Lumped-parameter and distributed-parameter visualization of a distillation tray. (a) Actual plate with complex flow patterns and resulting variations in properties from point to point. (b) Idealized equilibrium stage ignoring all internal variations.

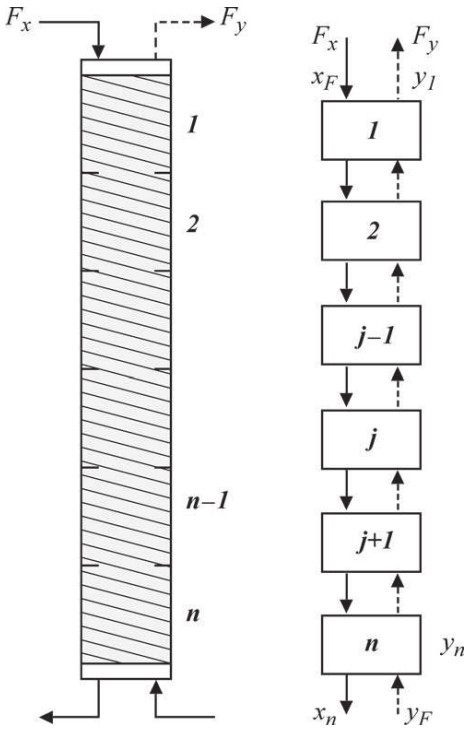

Figure 2.2. Continuous versus discrete modeling of a packed column absorber.

models in which a concentration is uniform at each stage but differs from stage to stage in discrete jumps. Continuous models are described by differential equations and discrete models by difference equations. Figure 2.2 illustrates the two configurations.

The left-hand figure shows a packed column modeled as a continuous system, whereas the right-hand figure represents the column as a sequence of discrete (staged) units. The concentrations in the left-hand column would be continuous variables; those in the right-hand column would involve discontinuous jumps. The tic marks in the left-hand column represent hypothetical stages for analysis. It is, of course, possible to model the packed

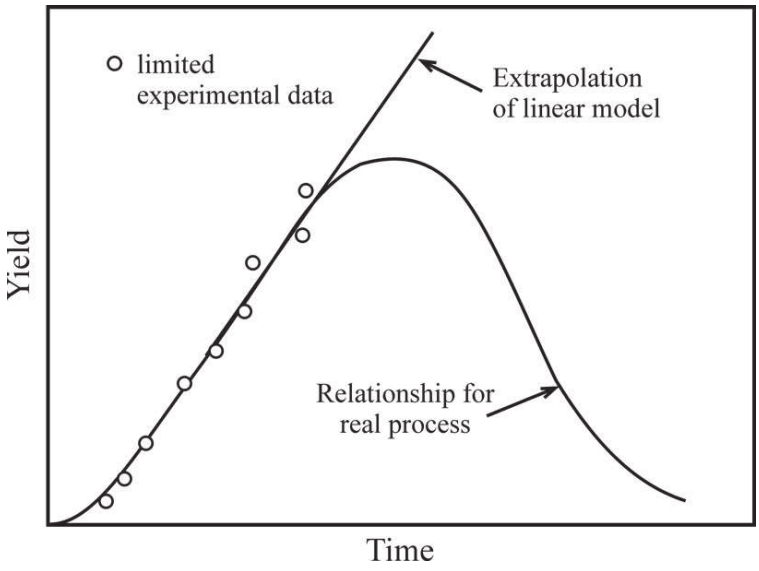

Figure 2.3. Danger of extrapolation. Yield of a chemical reactor versus time.

column in terms of imaginary segregated stages and to treat the plate column in terms of partial differential equations in which the concentrations are continuous variables.

Deterministic versus stochastic

Deterministic models or elements of models are those in which each variable and parameter can be assigned a definite fixed number, or a series of numbers, for any given set of conditions, i.e. the model has no components that are inherently uncertain. In contrast, the principle of uncertainty is introduced in stochastic or probabilistic models. The variables or parameters used to describe the input–output relationships and the structure of the elements (and the constraints) are not precisely known. A stochastic model involves parameters characterized by probability distributions. Due to this the stochastic model will produce different results in each realization.

Stochastic models play an important role in understanding chaotic phenomena such as Brownian motion and turbulence. They are also used to describe highly heterogeneous systems, e.g. transport in fractured media. Stochastic models are used in control theory to account for the irregular nature of disturbances.

In the present context, we will focus upon deterministic models.

Interpolation versus extrapolation

A model based on interpolation implies that the model is fitted to experimentally determined values at different points and that the model is used to interpolate between these points. A model used for extrapolation, in comparison, goes beyond the range of experimental data.

Typically, thermodynamic models are used for interpolation as well as correlations in complicated transport phenomena applications. Extrapolation requires, in general, a detailed mechanistic understanding of the system. The procedure requires great care to avoid misleading conclusions. Figure 2.3 illustrates an exaggerated case of extrapolation

by means of a linear model into a region beyond the range of experimental data for a chemical reaction that reaches a maximum yield in time.

In the safety analysis of nuclear waste repositories models are used to predict the fate of leaking radionuclides into the surrounding rock formation over geological time scales. Naturally, it is of the utmost importance that these models are physically/chemically sound and based on well-understood mechanistic principles.

Mechanistic versus empirical

Mechanistic means that models are based on the underlying physics and chemistry governing the behavior of a process; empirical means that models are based on correlated experimental data. Empirical modeling depends on the availability of process data, whereas mechanistic modeling does not; however, a fundamental understanding of the physics and chemistry of the process is required. Mechanistic models are preferably used in process design, whereas empirical models can be used when only trends are needed, such as in process control. Semi-empirical models cover the range in between. This discussion closely resembles the one regarding extrapolation/interpolation.

Coupled versus not coupled

When a model consists of two or more interacting relations, we have a coupled model. The coupling may be weak or strong. If the interaction only works in one direction, we speak of weak coupling (one-way coupling); if it operates in both directions we speak of strong (two-way) coupling. Forced convection is an example of one-way coupling, and free convection is an example of two-way coupling. In forced convection, the flow field is independent of the transport of energy and can be solved first and then introduced into the energy equation. In free convection, flow and energy transport are intimately coupled since the flow is generated by density differences originating from temperature differences. A model of a pneumatic conveying dryer involves a high degree of coupling (see Example 1.1).

2.2 Classification based on mathematical complexity

Another classification scheme to be considered is shown in Figure 2.4.

It can be seen that the complexity of solving a mathematical problem roughly increases as we go down Figure 2.4. In other words, algebraic equations are usually easier to solve than ordinary differential equations, which in turn are usually easier to solve than partial differential equations. This is not always true, of course, since a linear partial differential equation may be easier to solve than a non-linear ordinary differential equation. The accuracy of the representation of the actual physical system attained using the mathematical model also roughly increases as we go down the table, because the more independent variables and parameters that are taken into account, the better the mathematical model will be.

The theory of ordinary differential equations is reasonably well advanced with regard to analytical solutions, but the same is not true for the theory of partial differential

Table 2.1. Classification of mathematical problems and their ease of solution using analytical methods

	Linear equations			Non-linear equations		
Equation	One equation	Several equations	Many equations	One equation	Several equations	Many equations
Algebraic	trivial	easy	essentially impossible	very difficult	very difficult	impossible
Ordinary differential	easy	difficult	essentially impossible	very difficult	impossible	impossible
Partial differential	difficult	essentially impossible	impossible	essentially impossible	impossible	impossible

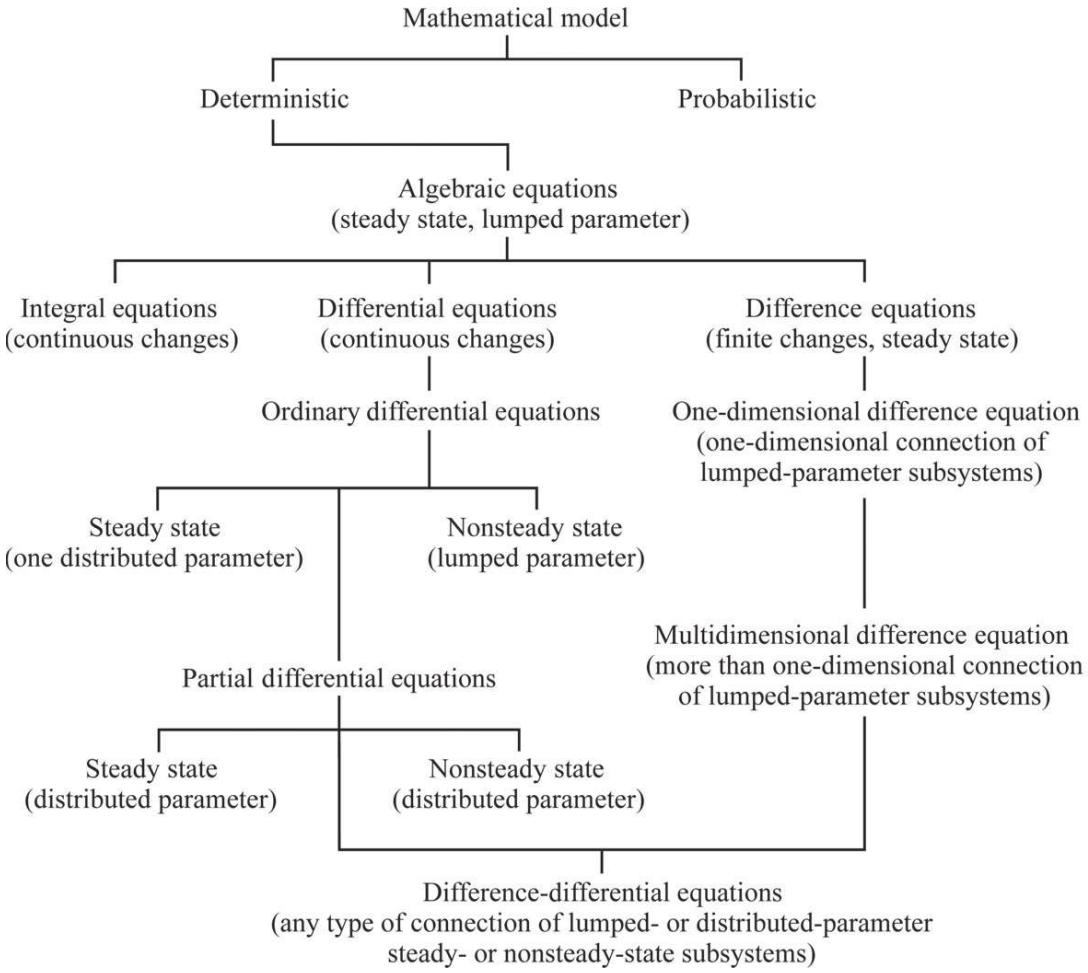

Figure 2.4. Classification based on mathematical complexity.

equations. Thus we can rather seldom find the analytical solution to a partial differential equation, and, in fact, when we do, it very often involves such things as infinite series, which are sometimes difficult to handle computationally. Table 2.1 shows the various classes of mathematical equations and the limited class amenable to analytical solution.

It should be noted that, in a model with more than one equation, the difficulty in obtaining a solution is dependent on the degree of coupling.

Table 2.2. Classification of models according to scale

Level of physicochemical description	Topical designations	Parameters
Molecular	treats discrete entities; quantum mechanics, statistical mechanics, kinetic theory	distribution functions; collision integrals
Microscopic	laminar transport phenomena, statistical theories of turbulence	phenomenological coefficients; viscosity, thermal conductivity, diffusivity
Mesoscopic	laminar and turbulent transport phenomena; transport in porous media	"effective" transport coefficients
Macroscopic	process engineering, unit operations	interphase transport coefficients

A model formulated in terms of differential equations can often be rephrased in terms of integral equations (and vice versa) so that many additional models are essentially included in this classification scheme. Difference equations account for finite changes from one stage to another and have significance parallel to that given above for (continuous) differential equations.

The classification scheme given in Table 2.1 for *analytical* methods has its counterpart for *numerical* methods. In such a case, the borderline to difficult/impossible problems is shifted to the right. In most cases, the models need to be solved numerically. Some reasons for this might be non-linearities, varying material properties, and varying boundary conditions. Luckily the computational power available in modern computers seldom conflicts with the requirement of solving the model equations numerically.

2.3 Classification according to scale (degree of physical detail)

Physicochemical models based on the degree of internal detail of the system encompassed by the model are classified in Table 2.2. The degree of detail about a process decreases as we proceed down the table.

Molecular description

The most fundamental description of processes, in the present context, would be based on molecular considerations. A molecular description is distinguished by the fact that it treats an arbitrary system as if it were composed of individual entities, each of which obeys certain rules. Consequently, the properties and state variables of the system are obtained by summing over all of the entities. Quantum mechanics, equilibrium and non-equilibrium statistical mechanics, and classical mechanics are typical methods of analysis, by which the properties and responses of the system can be calculated.

Microscopic description

A microscopic description assumes that a process acts as a continuum and that the mass, momentum, and energy balances can be written in the form of phenomenological equations. This is the "usual" level of transport phenomena where detailed molecular

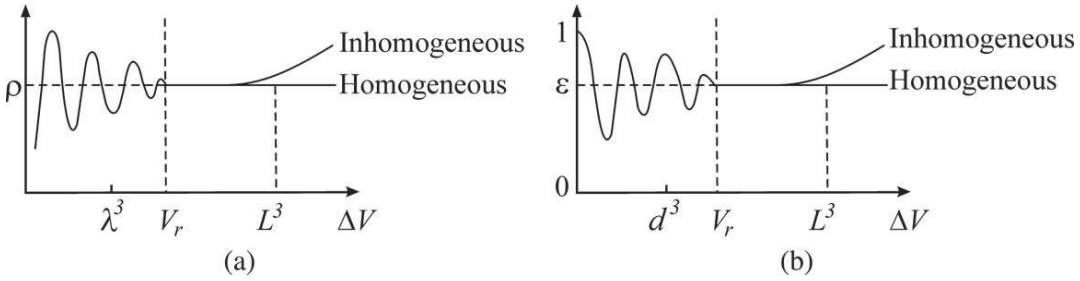

Figure 2.5. Concept of representative elementary volume for a fluid (a) and a porous medium (b), respectively.

interactions are ignored and differential balance equations are formulated for momentum, energy, and mass.

The continuum concept is illustrated in Figure 2.5(a) with the density of a fluid. The density, ρ, at a particular point in the fluid is defined as

$$\rho = \lim_{\Delta V \to V_r} \frac{\Delta m}{\Delta V}, \tag{2.1}$$

where Δm is the mass contained in a volume ΔV, and V_r is the smallest volume (the representative elementary volume) surrounding the point for which statistical averages are meaningful (in the figure, λ is the molecular mean free path and L is the macroscopic length scale). For air at room temperature and atmospheric pressure, the mean free path, λ, is approximately 80 nm. The concept of the density at a mathematical point is seen to be fictitious; however, taking $\rho = \lim_{\Delta V \to V_r}(\Delta m/\Delta V)$ is extremely useful, as it allows us to describe the fluid flow in terms of continuous functions. Note that, in general, the density may vary from point to point in a fluid and may also vary with respect to time.

Mesoscopic description

The next level of description, mesoscopic, involves averaging at higher levels and thus incorporates less detailed information about the internal features of the system of interest. This level is of particular interest for processes involving turbulent flow or flow in geometrically complex systems on a fine scale, such as porous media. The values of the dependent variables are averaged in time (turbulence) or space (porous media). Processes at this level are described by "effective" transport coefficients such as eddy viscosity (turbulence) or permeability (porous media).

The continuum concept at the porous media level is illustrated in Figure 2.5(b) for porosity:

$$\varepsilon = \lim_{\Delta V \to V_r} \frac{\Delta V_v}{\Delta V}, \tag{2.2}$$

where ΔV_v is the void volume in ΔV, and d is the pore length scale.

Time averaging in turbulence is illustrated in Figure 2.6.

The instantaneous velocity v_z oscillates irregularly. We define the time-smoothed velocity $\overline{v}_z$ by taking a time average of v_z over a time interval t_0, which is large with respect to the time of turbulent oscillation but small with respect to the overall time

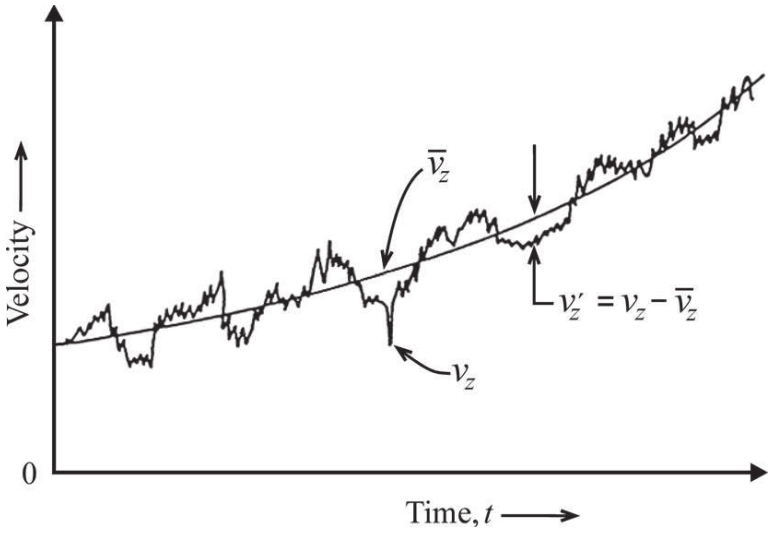

Figure 2.6. Time averaging.

changes:

$$\overline{v}_z = \frac{1}{t_0} \int_t^{t+t_0} v_z \, dt. \tag{2.3}$$

Macroscopic description

The final level, macroscopic, ignores all the details within a system and merely creates a balance equation for the entire system. The dependent variables, such as concentration and temperature, are not functions of position, but represent overall averages throughout the volume of the system. The model is effective as long as detailed information internal to the system is not required in model building. Macroscopic and lumped mean the same thing.

In science, events distinguished by large differences in scale often have very little influence on one another. The phenomena can, in such a case, be treated independently. Surface waves in a liquid, for instance, can be described in a manner that ignores the molecular structure of the liquid. Almost all practical theories in physics and engineering depend on isolating a limited range of length scales. This is why the kinetic theory of gases ignores effects with length scales smaller than the size of a molecule and much larger than the mean free path of a molecule. There are, however, some phenomena where events at many length scales make contributions of equal importance. One example is the behavior of a liquid near the critical point. Near that point water develops fluctuations in density at all possible scales: drops and bubbles of all sizes occur from single molecules up to the volume of the specimen.

2.4 Questions

(1) What is the difference between a lumped- and a distributed-parameter model?

(2) Explain the difference between deterministic and stochastic models.

(3) Why is a linear mathematical model tractable for analytical solution?

(4) Describe the continuum concept.

(5) At what scale is Darcy's law formulated? Are there alternatives that describe flow in porous materials?

3 Model formulation

Formulating mathematical models by applying balance and conservation principles and constitutive relations for fluxes is the topic of this chapter. The aim is to give the reader tools and skills for:

- constructing models using balances on differential or macroscopic control volumes for momentum, heat, mass, and numbers (population balances);
- constructing models by simplifying general model equations.

3.1 Balances and conservation principles

Before formulating a model it is crucial to define the system boundary. The purpose of the boundary is to define the system in relation to its surroundings. In Figure 3.1, a stirred tank is isolated from its surroundings by the dashed circle. All significant phenomena enclosed within this boundary need to be included in a successful model. The system boundary may be chosen in different ways, but for most systems the boundary to use is natural. Models derived from physicochemical principles are usually based on the general balance concept:

$$\begin{bmatrix} accumulation \\ within\ system \end{bmatrix} = \begin{bmatrix} net\ transport\ in \\ through\ system \\ boundaries \end{bmatrix} + \begin{bmatrix} net\ generation \\ within\ system \end{bmatrix}.$$

This relation is very general. The objective of model building is to transform the verbal concept into mathematical statements that are specific to the quantity of interest. We may balance mass, energy, and momentum as well as, for example, entropy and countable entities such as size and age distributions (population balances). Some of these entities are conserved, for example total mass, whilst some are not, for example the mass of a species in a mixture (due to chemical reactions).

By using the balance principle, we can derive model equations by balancing the quantities within the defined system boundary. A few examples of important balance equations are given in the following.

Overall (total) mass balance

The overall total mass balance describes the total mass in a system. Obviously there can be only one total mass balance equation, and the net generation term is zero, which means that mass is a conserved quantity.